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Discovery

Occurrence, fate and removal of emerging contaminates in a hybrid constructed wetland treating greywater

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ABSTRACT

Emerging contaminants (ECs) are chemicals that are discovered or detected recently in the water and wastewater systems and are often considered as endocrine disruptors. ECs are one of the main constituents of products used in day to day life, such as pharmaceutical, surfactants, personal care products, plasticizers and other additives. Earlier studies suggested that these compounds persist in environment for longer time and can be toxic to humans and ecosystem. In order to remove such ECs, advanced treatment techniques such as ozonation, photo-Fenton process and membrane reactors are being used. However, most of these technologies require large capital investment and high operation and maintenance costs. Hence, it is essential to find a sustainable treatment

system for the removal of EC from wastewater treatment systems. In this study, the removal of surfactants and personal care products such as sodium dodecyl sulphate (SDS), propylene glycol (PG) and trimethyl amine (TMA) from greywater using a hybrid constructed wetland (HYCW) was evaluated. The pilot scale HYCW system planted with *Phragmites australis* was of 10.1 m x 2.55 m x 1.3 m in size and was fed continuously with greywater from November 2013 until May, 2015 with a flow rate of 2.5 cu. m/ day. The water tight treatment basin consisted of a series of baffle walls. It was observed that HYCW was able to remove the target pollutants effectively. The concentrations of SDS reduced from 15.22 ± 12.22 mg/L to 0.32 ± 0.8 mg/L (94 - 98%); PG: 46.28 ± 26.24 to 2.72 ± 0.9 mg/L (95-98%) and TMA: 8.28 ± 7.22 mg/L to 0.14 ± 0.64 mg/L (95-99%). The effluent form HYCW was able to meet the USEPA regulatory discharge limits of the target pollutants for reuse in irrigation and toilet flushing.

Keywords: Emerging contaminants, constructed wetland, hybrid, surfactants, personal care products.

1. INTRODUCTION

Water shortage, poor quality of water and water related diseases are the worldwide problems which need to be resolved to provide safe and uninterrupted water for human use. The rising demand for fresh water has increased the stress of surface and groundwater resources. A better way to mitigate water scarcity is by treating and reusing greywater as non-potable water (irrigation, toilet flushing, floor/car washing etc) (Santos et al., 2012; Chin et al., 2009; Barisci et al., 2015). Greywater is the type of wastewater collected from all sources (showers, washing machine etc.,) except toilet. The separation and treatment of grey water and black water is increased significantly (Santos et al., 2012). Greywater constitutes 50-80% of the total household wastewater (Barisci et al., 2015).

The main contamination in greywater is caused by detergents, personal care products (PCPs), dirt and filths in clothes and body oils (Ramona et al., 2004). Many technologies are available including physical, chemical and biological systems. All these systems are effective in treating the organic, nutrient and bacterial contamination. However, many a times greywater is contaminated with organic xenobiotic compounds like surfactants and PCPs in concentration ranges of µg to mg level (Grundwasser et al., 1998; Ternes 1998). Surfactants and PCPs are extensively used in washing processes, and are currently classified as emerging contaminants (ECs) or endocrine disruptive compound. The surfactants are classified based on the functional group attached to it as cationic, anionic, non-ionic and amphoteric. The sodium do-decyl sulphate (SDS), an anionic surfactant of 28%, and propylene glycol (PG), a non-ionic surfactant of 5% and tri-methyl amine, a cationic surfactant of 7% were predominantly used in detergents and soaps.

The conventional treatment systems are not capable of removing these surfactants and PCPs. As a result, these pollutants are present in the discharged environment like groundwater, soil etc. To remove such trace contaminates from wastewater, advanced technologies like membrane filter, advance oxidation process etc are required. These treatment systems are expensive and require huge capital investment and uninterrupted power supply (Petrovic et al., 2003). Constructed wetlands (CWs) require low operational and maintenance cost as it does not require mechanical or electrical components. CWs are simple to operate and robust natural treatment processes. In addition they add aesthetics to the location (Tanner et al., 2012). Constructed wetlands are classified based on flow direction as horizontal subsurface flow (HF) and vertical subsurface flow systems (VF). HF system are effective in denitrification due to their low oxygen content, and VF are good in nitrification due to aerobic condition prevailing. Henceforth, the strengths of HF and VF system are combined in hybrid system (Cooper, 1999; Masi and Martinuzzi, 2007; Vymazal, 2007).

Many reports are available regarding the use of hybrid constructed wetlands (HF followed by VF or VF followed by HF combinations) for the removal of organic, nutrients and solids. However, only a few studies have carried out to evaluate the potential of constructed wetland systems to remove EC's from domestic wastewater. These studies were conducted in systems consisting of a single wetland configuration at a time, namely VF, HF (Matamoros et al., 2009) or free water surface (FWS) (Llorens et al., 2009 and Matamoros et al., 2009). But no studies are carried until now to understand the removal of surfactants and personal care product (PCP's) from grey water, in a single stage hybrid constructed wetland system. This study focused on the treatment of surfactants and PCPs (SDS, PG and TMA) present in greywater by a novel hybrid constructed wetland system under different operating conditions.

2. MATERIALS AND METHODS

2.1. Analytical Chemicals

A standard salt of sodium lauryl sulphate (SDS) was purchased from Rankem chemicals, India; a standard solution of propylene glycol (PG) was purchased from Fischer chemicals, India; and tri-methyl amine (TMA) was purchased from Merck chemicals, India. N-hexane (HPLC grade) and toluene (99% pure), the extractions solutions used in the present study, were procured from Rankem

chemicals, India. The acridine orange used as a dying pigment was procured form Loba chemicals, India, and glacial acetic acid (99%), used as an acidifying agent was purchased from Rankem chemicals.

2.2. Analytical Methods

Sodium do-decyl sulphate (SDS) was analyzed calorimetrically at 467 nm by UV 1800 spectrophotometer (Shimadzu, Japan). The samples were first acidified with glacial acetic acid, acridine orange was used for dying pigment, and toluene was used for extraction. The toluene layer is discarded and aqueous layer was used for further analysis (Adak et al., 2005). Propylene glycol (PG) and tri-methyl amine (TMA) were analyzed using PerkinElmer Clarus 500, USA gas chromatograph fitted with flame ionization detector (GC-FID). The column used was PE – 624, 30 m x 0.53 mm x 0.5 mm thickness. The samples were extracted by n-hexane with the ratio of 1:1, and were analyzed in GC-FID with injector temperature of 60 °C, oven temperature of 250 °C and column temperature of 280 °C using high pure nitrogen as carrier gas at a flow rate of 1 mL/min. The other physico-chemical and biological parameters were analyzed as per standard methods (APHA, 2005).

2.3. Pilot scale constructed wetland

A novel baffled type (hybrid) pilot scale subsurface flow constructed wetland planted with *Phragmites australis* (10.1 m x 2.55 m x 1.2 m) were designed and constructed inside the campus (Figure 1(a)). The wetland was fed with a real time greywater collected from 60 person's bathrooms with a flow rate of 2.5 cu. m/ day. The flow of greywater was diverted inside the tank by providing cemented baffle walls as shown in Figure 1(b), to have a continuous up-flow and down flow movement of wastewater. The entire tank was lined with cement concrete to avoid the contamination of groundwater. The tank was filled with < 10 cm gravel at the bottom 30 cm, and the top 60 cm was filled with a 50:50 mixture of sand and brick bat. A well grown shoot of *Phragmites australis* with 5 cm height was planted above the sand filling at a density of 6 plants per sq. m.

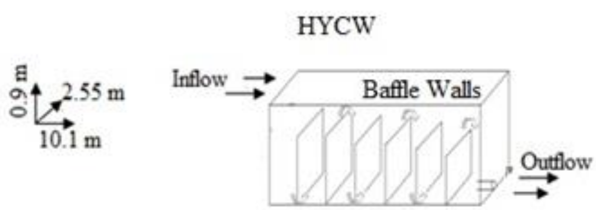

Figure 1(a) Schematic representation of Hybrid constructed wetland

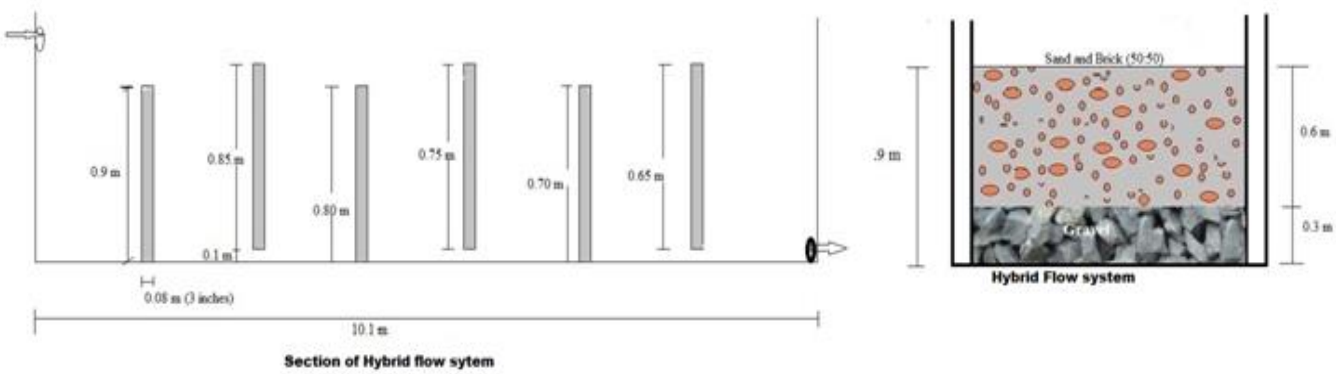

Figure 1 (b) Cross sectional view of Hybrid constructed wetland

2.4. Operation and Monitoring

The hybrid constructed wetland was operated more than 2 years from November, 2013 to May 2015, with continuous flow of greywater. The performance of CW was evaluated weekly once by collecting the water samples from both the inlet and outlet, and analyzed for the target pollutants (SDS, PG and TMA). The plants were harvested once (October, 2014) during the entire period of study. The CW was evaluated under different operating conditions.

3. RESULTS AND DISCUSSION

3.1. Grey water characteristics

During the sampling period (2013-2015), samples were collected from both inlet and outlet every week and analyzed for SDS, PG,TMA, BOD, COD, TSS, NO_3 – N, TP and fecal coliforms (FC) (APHA, 2005). The average inlet and outlet concentrations of each parameter are tabulated in Table 1 with standard limits for reuse as prescribed by USEPA. The raw greywater characterization was comparable with the earlier reported values except the fecal coliforms (Mohamed et al., 2014). The FC value was lower than the reported value. The micro pollutants (SDS, PG and TMA) concentrations were slightly higher than the earlier reported values (Zapater et al, 2011). This may be due the large quantity of water coming from washing machines and no contribution from kitchen or dining facility.

Table 1 Greywater characteristics

Parameters	Raw Sample	Standard limits for toilet flushing and reuse
pH	7.24 - 8.34	5.5 to 9.0
COD (mg/L)	216 - 240	10
BOD (mg/L)	72 - 80	100
TSS (mg/L)	240 - 280	30
TOC (mg/L)	23 -36.48	NA
TN (mg/L)	17 - 28.82	NA
NO_3 – N (mg/L)	12.32 -17.84	10
TP (mg/L)	2.93 – 3.84	5
NH_4 – N (mg/L)	10.28 -14.56	50
MPN – FC cfu / 100 mL	50 - 120	No detectable / 100 mL
SDS (mg/L)	14.99 – 35.89	1
PG (mg/L)	11.58 - 46.59	NA
TMA (mg/L)	8.67 - 15.54	NA

3.2. Removal of surfactants and personal care products in HYCW

Concentrations of the targeted pollutants (SDS, PG and TMA) in the influent and the outlet of hybrid system are shown in Table 1. The target pollutants removal rate was constant throughout the study period (85-98%). The higher removal rate of surfactants and PCPs in the hybrid constructed wetland was mainly due to high HRT (12.5 days –16.5 days). Additionally, the up-flow and down flow increased the contact between the pollutants, the plants and media (Zwiener and Frimmel, 2003; Yu et al., 2009). In addition, when hybrid system was compared with other advanced treatment system like ozonation (Zwiener and Frimmel, 2003) or membrane bio-reactors (MBR) (Kimura et al., 2009), the removal rate of surfactants and PPCPs were comparable. The removal rate of SDS (high K_{ow}) in HYCW was found to be high (85-94%). This may be due to adsorption and bacterial degradation. The PG and TMA (low K_{ow} and highly soluble) were removed by plant uptake (Zhang et al., 2012). The removal rate of SDS were comparatively more than PG and

TMA during the start-up phase, as the proliferation of microbes and plants have just started and adsorption was the predominant mechanism for removal.

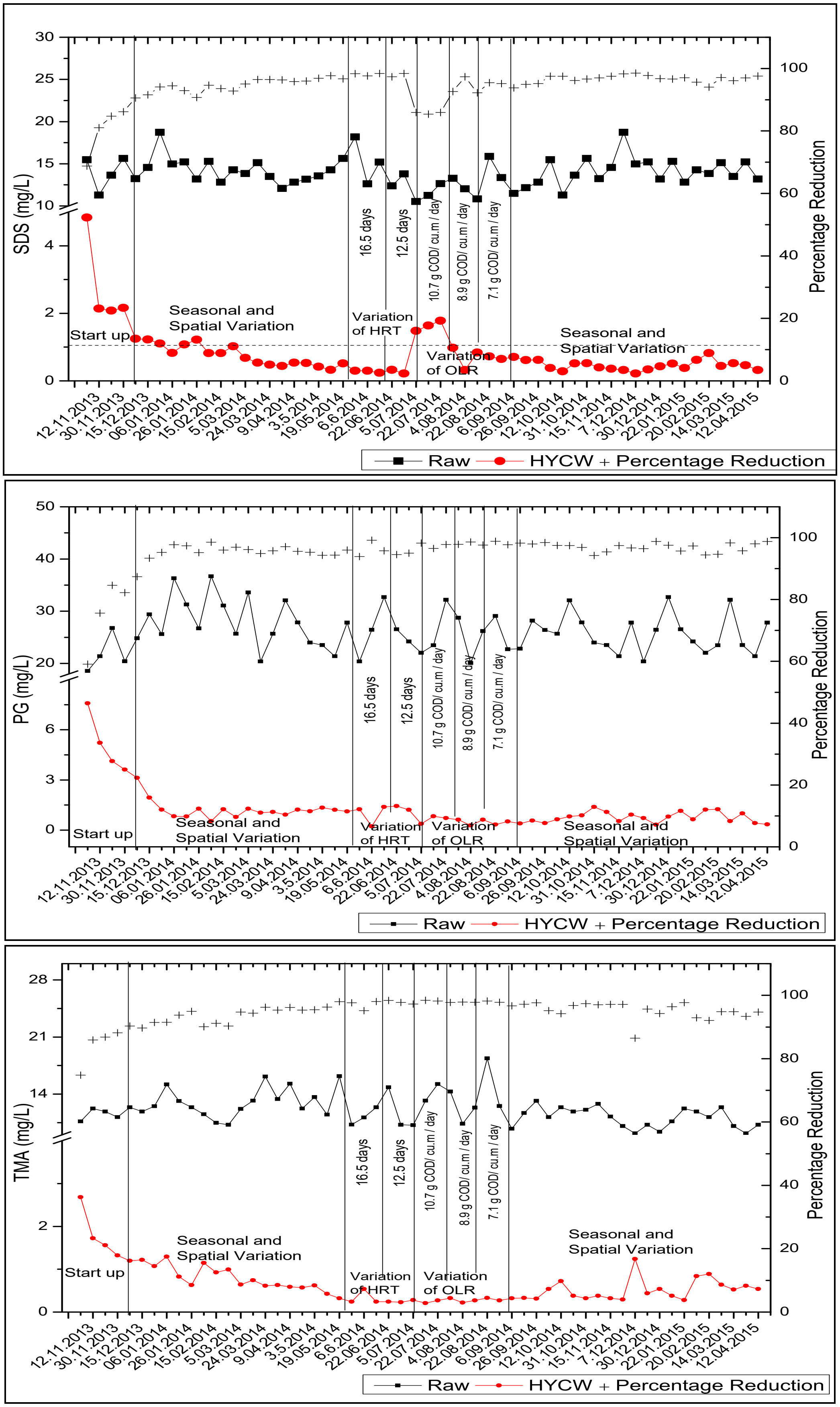

Figure 2 Performance of HYCW under various operating conditions

3.3. Seasonal Variation / Effect of temperature

The elimination rate of SDS, PG and TMA in the hybrid constructed wetland during monsoon and summer was examined. It was generally found that the pollutants removal efficiency was greatly affected by seasons or water temperature. The seasonal variability was mainly attributed to two main physical conditions, namely solar radiation and water temperature. Low temperatures decrease the bio-degradation kinetics and low sun irradiation decreases the phytodegradation rates. As expected, compounds that require longer time for biodegradation and/or phytodegradation were affected by seasons (i.e. SDS, PG and TMA) (Simonich et al., 2002). Sodium dodecyl sulphate, highly hydrophobic compound (K_d > 3.6) (Hansch et al., 1996) are removed better during summer than winter season. The compounds (PG and TMA) that are highly water soluble was also affected by seasons, as the predominant mechanism for the removal of pollutants are mostly by plant uptake and biodegradation. Hence, the removal efficiency was more during summer than in winter or monsoon.

3.4. Effect of hydraulic retention time

In most of the treatment systems, the treatment efficiency decreases with increase in either hydraulic or organic loading. The concentration of all pollutants in the effluent increased for the HRT of 12.5 days with removal efficiency of 86%, with further increase in HRT to 16.5 days the removal efficiency increased to 96%. SDS, which is considered as a hydrophobic compound was predominantly removed by microbial degradation and adsorption to soil. The results obtained showed a good agreement with those obtained by Langford et al., (2005). In case of PG and TMA, the change in HRT had no effect on the removal efficiency (at 12.5 days, PG was 90% and TMA was 92% removed; at 16.5 days, PG was 92% and TMA was 92% removed) (Figure 2). The probable reason being, both PG and TMA are water soluble compounds and are predominantly removed by the plant uptake. Changes in HRT do not affect the plant uptake rate for water soluble compounds as found by Akratos and Tsihrintzis, 2007.

3.5. Effect of organic loading rate

It was observed that as the OLR increased from 7.1 g COD/ cu. m/ day to 10.7 g COD/ cu. m/ day, the removal efficiency decreased as shown in Figure 2. The SDS removal efficiency was found to be 92% during 7.1 g COD/cu. m/ day and has reduced to 82% during 10.7 g COD/ cu. m/ day. Similar trend was observed for PG and TMA compound. Due to addition of external carbon source, the degradation rates of organic pollutants were hindered. Sucrose is a readily biodegradable compound than SDS, PG and TMA. Therefore, microbial consortia would have utilized more sucrose as a carbon source than the target pollutant. As a result, lesser biodegradation was observed for target pollutants with increase in OLR. Similar trend was reported by other researchers also (Nyberg et al., 1992).

4. CONCLUSION

Surfactants and personal care products (SDS, PG and TMA) are present in raw greywater at high concentration (14.99 – 35.89 mg/L for SDS; 11.58 - 46.59 for PG and 8.67 - 15.54 for TMA). It was observed that the hybrid constructed wetland was able to remove these compounds effectively. The pollutant concentrations in treated water were in the order of 0.32±0.82 mg/L 2.72±0.96 mg/L and 0.14±0.64 mg/L for SDS, PG and TMA respectively. The reasons for higher removal of ECs are mainly due to the higher hydraulic retention time (HRT) (12.5 -16.5 days). It is also observed that the removal efficiencies are highly depended on temperature and sun irradiation. The results of this study clearly demonstrate that the hybrid wetland was able to remove emerging contaminants effectively

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